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STUDIES OF THE VOLTAMMETRIC DETERMINATION OF TRACE
METALS IN SEAWATER(0) CALIFORNIA UNIV SANTA CRUZ CENTER
FOR COASTAL MARINE STUDIES K W BRULAND NOV 82

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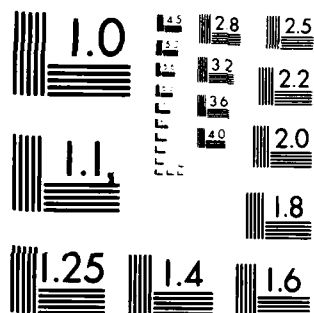
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FINAL TECHNICAL REPORT

OF

ONR CONTRACT #N00014-82-K-0029

"Studies of the Voltammetric Determination of Trace Metals in Seawater"

Period 15 Nov 81 through 15 Nov 82; \$26,601

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Both the Principal Investigator and K. H. Coale have been funded by the Office of Naval Research to study voltammetry for six months (spring and summer, 1982) in the laboratories of Professor H. W. Nürnberg (also with Dr. L. Mart and Dr. Valenta) at the Institute for Applied Physical Chemistry at KFA, Jülich, F.R. Germany (4½ months), and with Professor J.C. Duinker (also with K. Kramer) at the Netherlands Institute for Sea Research in Texel, The Netherlands (1 month). Our visit and collaboration with these research groups has provided us with the expertise to develop a shipboard multi-electrode, differential-pulse anodic-stripping voltammetry (DPASV)

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system to determine Cu, Pb, Cd, and Zn at open ocean concentrations, and also Ni and Co by DPV after interfacial adsorption of their dimethylglyoxime chelates.

During our stay with Professor Nürnberg's group there was a great deal of technical expertise to acquire; particularly in the area of electrode fabrication. These are mercury film electrodes formed in-situ at a rotating glassy carbon surface. Nürnberg's group fabricates their own "home-made" electrodes which are substantially more sensitive than any commercially available. Nürnberg and his research group have had decades of experience in voltammetric applications which were invaluable to us in our studies. Two collaborative efforts were undertaken with Nürnberg. One was a field expedition to the North Sea (early May 1982) where Dr. Leon Mart from Nürnberg's group and Kees Kramer from Professor Jan Duinker's group participated. We collected samples to be analyzed both by our standard organic extraction/graphite-furnace atomic absorption spectrometric methods, as well as their respective DPASV systems. This provided us with experience with such systems at sea, as well as an excellent intercalibration study. Secondly, we brought with us samples of a detailed profile from the North Pacific on which we had previously determined each of the metals by our current methods. We personally analyzed this profile on a DPASV system that we fabricated with Leon Mart during our stay in Juelich.

The time spent in The Netherlands with Professor Duinker's research group was primarily to gain additional expertise from another research group's perspective on their DPASV system and to finish the earlier collaborative study during the North Sea Cruise.

We are now back at UCSC with our initial ONR contract (investigating the feasibility of voltammetric methods) terminated. We are excited about

the potential applications of such an approach and, in fact, we have returned with an initial electrode system which we fabricated at Jülich with Dr. Leon Mart. We are convinced by the preliminary feasibility study that continuation of this research is desirable and justifiable. Subsequently, the P.I. has had discussions with Prof. M. Branica of Yugoslavia at the Gordon Research Conference on Chemical Oceanography. These discussions were fruitful and stimulating and we plan to continue interacting with both Professors Nürnberg and Branica.

III. BRIEF THEORY OF VOLTAMMETRY AS APPLIED TO THE MERCURY FILM ELECTRODE DPASV SYSTEM

The basic voltammetric cell consists of the analyte whose metal concentration is to be determined and three electrodes. During the cathodic deposition mode, metal ions are reduced by the potential at the working electrode and deposited on the mercury film at the electrode surface as a metal-Hg amalgam. The potential at the working electrode is induced by the polarograph through the counter electrode with the reference electrode taken as zero. The actual potential of the working electrode depends upon the type of reference electrode used. In our case the reference electrode is a Ag/AgCl electrode so that all potentials selected at the polarograph are relative to the Ag/AgCl electrode (with a potential of +0.20 V versus the normal hydrogen electrode; sat'd KCl and 23°C). In the anodic stripping mode, the potential at the working electrode is linearly ramped towards more positive potentials (at 10 mv/sec) during which time fixed height pulses (of +50 mv) are superimposed upon this ramping potential. The current flow is sampled just before application of the pulse and again at the end of the pulse with the readout to the recorder representing the difference between

these two currents. At given potentials, metals formed on the working electrode as metal-Hg amalgams, are re-oxidized and migrate from the electrode surface. This ion migration constitutes a current which is detected and has its differential signal recorded by the polarograph as a peak at the proper potential. The potentials of Zn, Cd, Pb and Cu are far enough apart to allow the simultaneous determination of each of these metals.

There are a variety of voltammetric approaches to determining these metals. However, at the ultra trace levels observed in oceanic waters we are limited to the rotating or vibrating glassy carbon electrodes with a thin Hg film operated with a cathodic deposition period required for the preconcentration of the trace metals, followed by anodic stripping in the differential pulse mode. The surface area of a thin mercury film formed on a 6 mm diameter glassy carbon electrode can approach 28 mm², compared with normal hanging mercury drop electrodes of only 2 mm². Additionally, the rotating or vibrating electrode system can optimize the mass transfer between the solution and electrode surface. All of these factors combine to yield the most sensitive voltammetric approach. Also of importance is that thin mercury-film electrodes have a substantially better resolution of current peaks than do hanging mercury drop electrodes (De Vries and Van Dalen, 1964; Roe and Toni, 1965).

Specific details of the detector fabrication, instrumental modifications, and operation of a thin-mercury film, rotating glassy carbon electrode (RGC), differential-pulse anodic-stripping voltammetry system are presented in Appendix A.

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IV. RESULTS OF THE INTERCOMPARISON STUDIES

The eventual goal of our voltammetric studies will be to characterize and quantify trace metal complexation with organic ligands in seawater. However, because of the controversial and confusing nature of this research topic, our philosophy is that we must approach this goal in logical steps; i.e. we must first prove we have the required sensitivity, accuracy, precision, and contamination control. The best way to demonstrate this level of competence is to determine by DPASV, the total dissolved metals on acidified (pH = 2) and at times U.V. oxidized samples that have been characterized by other independent methods (Bruland, 1980; Bruland et.al., 1979). During our stay in Professor Nürnberg's lab, we fabricated our own system and utilized it in a number of different intercomparison studies.

North Sea Intercomparison

On a research cruise to the central North Sea, we collected unfiltered surface samples from a raft, acidified them to pH 2 with Q-HCl, and stored them for analyses at KFA by DPASV and N10Z by our extraction/atomic absorption spectrometry techniques. The results are presented in Table 1. Our results with the DPASV method for both Cd and Cu as compared to the APDC/DDDC extraction/A.A. method agreed remarkably well. The precision was on the order of $\pm 4\%$. Lead results are not shown since there were no APDC/DDDC extraction results with which to compare them.

Russian Intercalibration Seawater Sample

The P.I. along with Mike Gordon and John Martin of Moss Landing Marine Laboratory were involved in an EPA sponsored intercalibration of a California Current surface water sample with some Soviet scientists. We

NORTH SEA INTERCOMPARISON Table 1

UCSC SURF RAFT UNFILTERED SAMPLES stored acidified with Q-HCl to pH 2.

The samples analyzed by DPASV were also U.V. oxidized.

	Cd ng·kg ⁻¹		Cu ng·kg ⁻¹	
	UCSC DPASV at KFA	APDC/DDDC ORG.EXT.at NIOZ	UCSC DPASV at KFA	APDC/DDDC ORG.EXT.at NIOZ
824016 (a)	34.6 ±1.4 (n=6)	32.2	362 ±20 (n=5)	330
(b)	33.6 ±1.3 (n=6)	33.3	368 ±10 (n=6)	333
(d)	33.6	--	392	--
824010 (a)	36.5	--	--	--
(c)	35.1	36.9	368	350
(d)	--	37.4	--	378

RUSSIAN INTERCALIBRATION SEAWATER SAMPLE Table 2

Stored acidified with HCl to pH ~ 1.5. The samples analyzed by DPASV were U.V. oxidized.

	UCSC DPASV at KFA	UCSC Org.Ext. A.A.	M.L.M.L. Org.Ext. A.A.
Cd	12.1 ±1.3 (n=7)	12.3 ±0.2 (n=6)	12.7 ±1.0
Pb	8.6 ±0.7 (n=4)	≤ 10	6*
Cu	72 ±2 (n=7)	70 ±2 (n=6)	66 ±3

* one sample by Chelex/A.A.

CANADIAN SEAWATER REFERENCE MATERIAL, NASS-1 Table 3

Stored acidified with HNO_3 to pH ~ 1.5 . The samples analyzed by DPASV were U.V. oxidized. Units in $\text{ng}\cdot\text{kg}^{-1}$.

	<u>UCSC DPASV at KFA</u>	<u>Current (May '82) best reliable value based on at least 2 independent methods</u>
Cd	33.0 \pm 2.3 (n=9)	29 \pm 4
Pb	31.8 \pm 2.0 (n=10)	39 \pm 6
Cu	107 \pm 6 (n=7)	99 \pm 10

brought this sample with us to KFA as a typical oceanic surface sample with substantially lower concentrations than observed in the North Sea. Table 2 presents the results. Again the excellent agreement between the two different methods implies a high degree of accuracy.

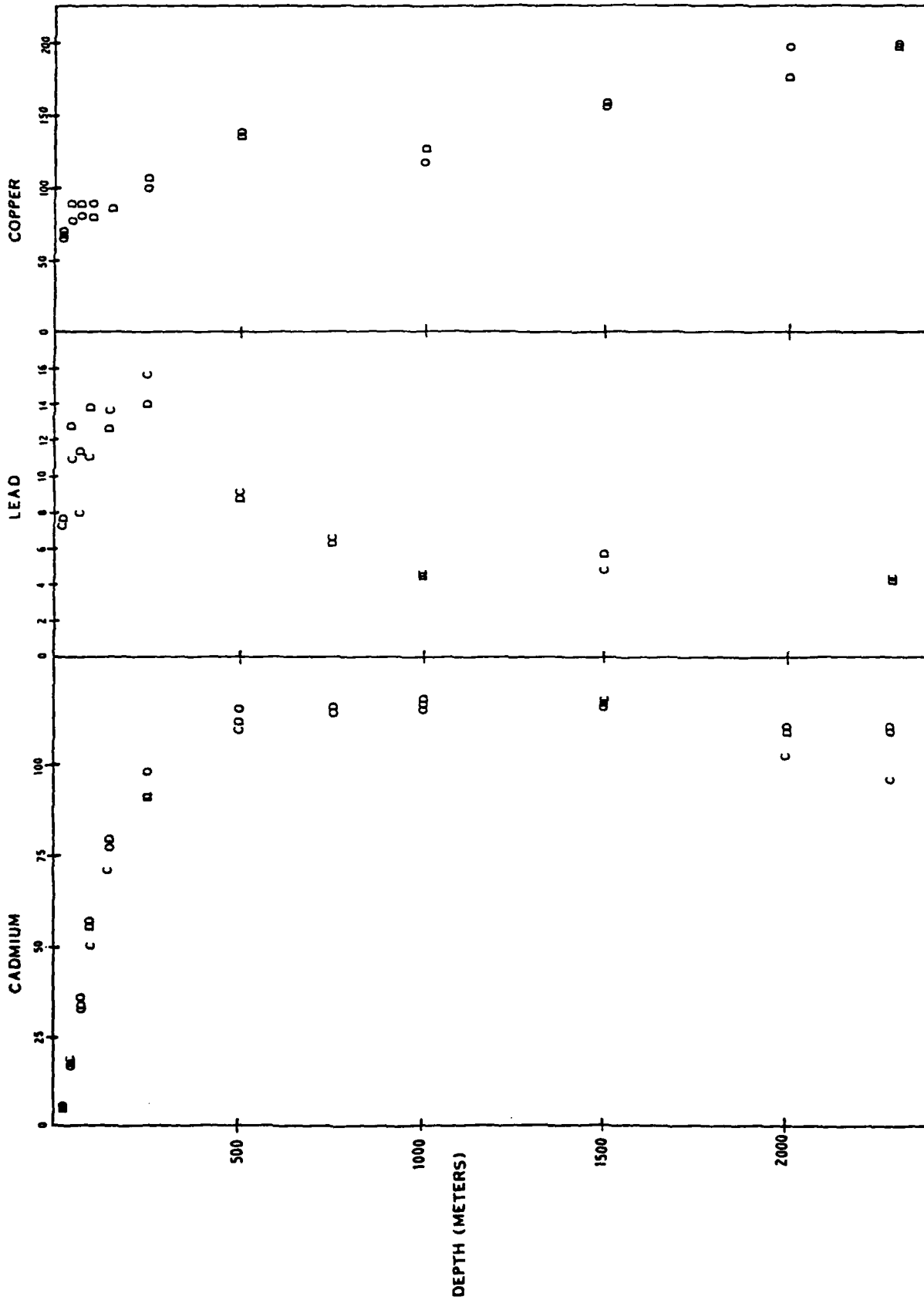
Canadian Seawater Reference Material, NASS-1

We obtained a sample of the new Canadian Reference seawater standard and analyzed it (Table 3). The agreement between our results and the current "best value" of the sample is within the potential error they list for their value.

VERTEX I Vertical Profile

We brought with us to KFA a vertical profile of filtered acidified seawater samples from our VERTEX I cruise from within the California Current. These samples had been previously analyzed at UCSC by both APDC/org. Extraction and Chelex ion exchange preconcentration followed by detection by atomic absorption spectrometry. The methods were similar to those used by Bruland (1980) and Bruland et.al. (1979). Figure 1 presents the results of the various methods plotted together. The results exhibit excellent agreement and demonstrate that the DPASV method has the precision, accuracy and sensitivity to determine these trace metals at their natural levels. Zinc was not analyzed on this profile because the samples were acidified to pH ~1.8 (zinc must be determined on samples at pH no lower than ~4 or 4.5 because of excessive hydrogen reduction at the electrode at low pH and the necessary cathodic deposition voltage for zinc).

The results of these intercomparison studies, together with a description of the new system fabricated at KFA are in a manuscript being



D - DPASV, O - ORG. EXT./A.A., C - CHELEX/A.A. UNITS IN NG/KG

Figure 1. Comparison of D.P.A.S.V. versus A.A. results on VERTEX-I samples.

prepared for publication in Analytical Chemistry (Bruland, Coale, Mart, Platzek, and Nürnberg, in prep).

It must also be added that the oceanographically consistent nature of the profiles in Figure 1 demonstrate that we have virtually eliminated contamination during the sampling, filtering, storage, and analysis stages. The importance of this cannot be underestimated.

REFERENCES

- Bruland, K.W. (1980) Oceanographic Distributions of Cd, Zn, Cu, and Ni in The North Pacific. *Earth Planet. Sci. Letters*, 47, 176-198.
- Bruland, K.W., R. Franks, G.A. Knauer, and J.H. Martin (1979) Sampling and Analytical Methods for the Determination of Cu, Cd, Zn, and Ni at the Nanogram per Liter Level in Seawater. *Analytica Chimica Acta.*, 105, 233-245.
- Bruland, K.W., K.H. Coale, L. Mart, U. Platzek and H.W. Nürnberg. Nano and Subnanomolar Determination of Cu, Cd and Pb in Seawater by DPASV - A Comparative Study. Manuscript in preparation.
- De Vries, W.T. and E. Van Dalen (1964) Theory of Anodic Stripping Voltammetry With a Plain, Thin, Mercury Film Electrode. *J. Electroanal. Chem.* 8 (1964), 366-377.
- Mart, L., H.W. Nürnberg and P. Valenta (1980) Prevention of Contamination and Other Accuracy Risks in Voltammetric Trace Metal Analysis of Natural Waters. Part III. Voltammetric Ultratrace Analysis with a Multicell System Designed for Clean Bench Working. *Fresenius Z. Anal. Chem. Bank 300* (1980), 350-362.
- Opekar, F. and P. Beran (1976) Rotating Disk Electrodes. Elsevier Sequoia S.A. 1976.
- Roe, D.K. and J.E.A. Toni (1965) An Equation for Anodic Stripping Curves of Thin Mercury-Film Electrodes. *Analytical Chemistry*, Vol. 37, No. 12 (1965), 1503-1506.

APPENDIX A:DETAILS OF THE ELECTRODE FABRICATION, INSTRUMENT
MODIFICATIONS, AND OPERATING PROCEDURES1. ELECTRODE FABRICATION

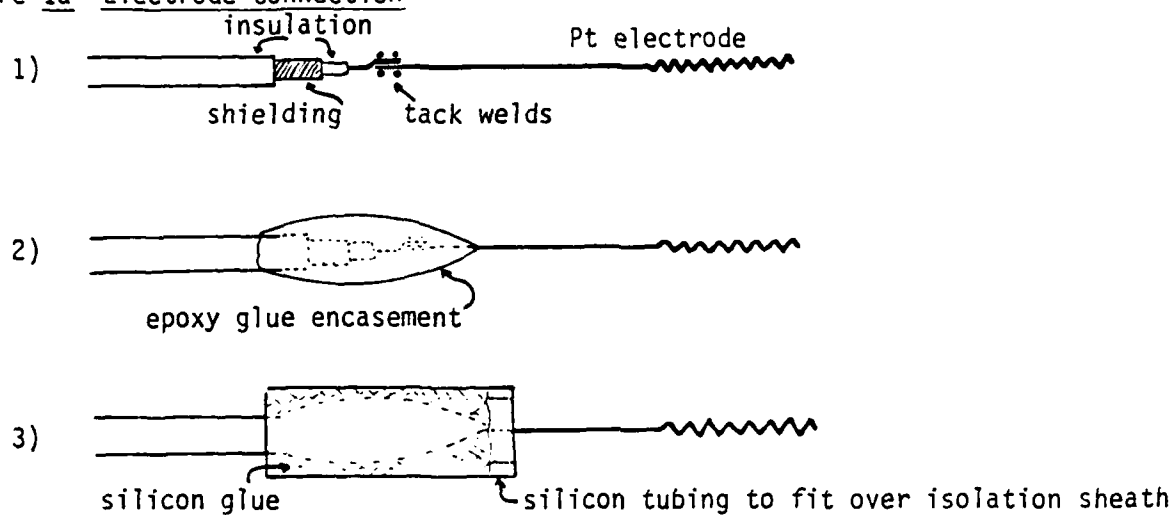
Ultra-trace metal determinations require that particularly special consideration be given to electrode fabrication and performance. A balance maximizing electrode performance yet minimizing risks due to contamination, has been achieved and is described below.

1a. Counter Electrode

Of the three electrodes, the counter electrode is the simplest to construct. In commercially available systems, this electrode often consists merely of a platinum wire immersed in the analyte and connected to the polarograph by means of an alligator clip. In the ultra trace range of metal determinations, this arrangement has drawbacks in that direct immersion of a platinum wire, not to mention the close proximity of an alligator clip to the sample constitutes a substantial contamination risk. In the system we constructed, (after Mart et.al. 1980), the counter electrode (a piece of acid cleaned coiled platinum wire) is isolated by enclosure in teflon tubing. Electrical contact to the solution is achieved by means of a porous Vicor^R tip (Corning Glass Corp., Cleveland), attached by means of heat shrinking teflon tubing. These Vicor tips (4 mm diam), have been shown to have an extremely low leakage rate yet still provide for a low ohmic resistance between sample and electrode. The tube containing the electrode is filled with a saturated KCl solution and electrical connection to the platinum wire is made by tack-welding the counter electrode to a shielded copper cable. This tack-welded juncture is incased in epoxy glue, silicon glue and silicon

tubing so that no bare wires or electrolytic products from the Pt-Cu junction can contaminate the electrolyte solution. This also structurally reinforces the connection (see Figure 1).

Figure 1a Electrode Connection



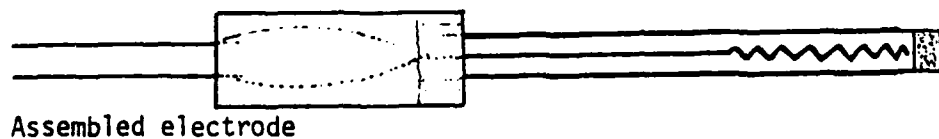
1b Teflon Isolation Sheath

1) heat shrink tubing, tip shrunk & Vicor tip inserted

2) teflon tubing inserted

3) heat shrunk electrode sheath, tip trimmed

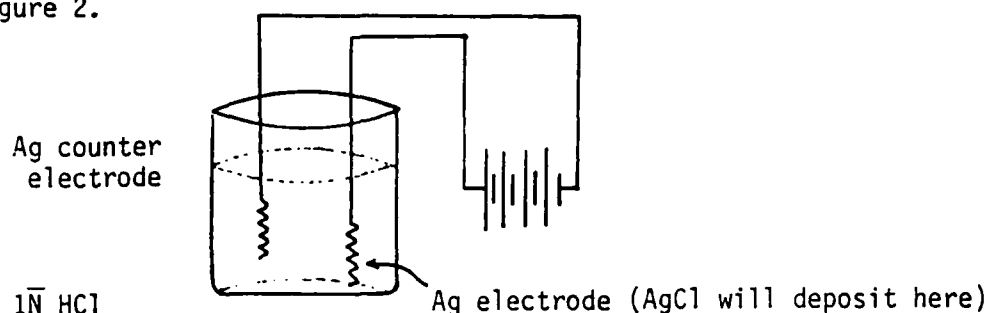
1c



1b. Reference Electrode

The reference electrode is fabricated in a manner identical to the counter electrode except that 1) a silver wire is used instead of a platinum wire and 2) the immersion tip of the silver wire is electrocoated with AgCl. This is accomplished by immersing the electrode tip in a 1N HCl solution with application of a $\sim +3$ volt potential to the silver wire for approximately 2 hrs. See Figure (2).

Figure 2.



A coating produced by such a treatment should last for hundreds of hours of analysis. The reference electrode is then sheathed in a manner identical to the counter electrode.

When preparing counter and reference electrode sheaths, the leakage rate of the Vicor tip should be tested during cleaning and before use. To do this, immerse the electrode sheaths in $\sim 3N$ HCl with their tips down and their open tops above acid level. Those sheaths whose interior acid level equilibrates rapidly with the exterior level (< 1 week) should not be used, as electrolyte leakage could contaminate the sample. Caution: once the Vicor tips are wetted, they should always be stored wet, as drying of the tips can increase the porosity and consequently, the leakage rate.

1c. Working Electrode

Commercially available electrodes are typically plagued with a variety of shortcomings such as poor sensitivity, high background noise due to faulty

or porous junctions between the glassy carbon and support material, or inferior quality of the glassy carbon itself. Even the smallest cracks or fissures in glued junctions or electrode surface can harbor polishing compound. This can lead to serious contamination problems which will preclude the determinations of metals such as Pb and Zn at natural oceanic levels. The hydrodynamic construction of most commercially available RGC electrodes has also been shown to effect poor mass transport of the solution towards the active electrode surface (Opekar and Beran, 1976) and inadequate precautions regarding electrode motor drivers have been known to lead to sample contamination (Mart et.al. 1980). For these reasons and others, it has become necessary to fabricate our own working electrodes.

The working electrode, although simple in principle is somewhat tedious to prepare as attention must be paid to the smallest details. The working electrode itself consists of a hollow plexiglass shaft with a glassy carbon disc imbedded in a plexiglass tip. This electrode is secured to a stainless steel axle which is connected to a motor. Although the axle is electrically isolated from the motor, electrical connection of the glassy carbon and the axle is made by mercury immersion of the axle tip within the electrode. Contact of the axle to the cable leading to the polarograph is made by mercury co-immersion of the mid-axle segment and a platinum cable lead. Both contacts assure low resistance and low noise junctions.

The fabrication of the electrode and motor drive assembly is described below: glassy carbon rod 6 mm in diameter (grade GC-A code EB-6 obtained from Tokai Carbon Company Ltd., Tokyo, Japan) should be cut into 8 mm long sections with lubricated diamond saw to avoid heating of the carbon. These sections are cleaned and must be treated so that they can be glued to the electrode tip. The glassy carbon sections are coated with Araldit B41 with

Härter Ht 901 from Araldit. The B41 component is heated on a beaker to 140°C then the appropriate weight percentage (100 B-41: 30 Ht-901) of the hardener Ht 901 is mixed in thoroughly and the mixture is allowed to stand a few minutes until all air bubbles have escaped. The glassy carbon sections, preheated to 140°C, are then immersed in the glue and allowed to soak for a few minutes before they are removed with plastic forceps and placed on a teflon support stand. Excess glue from coated glassy carbon sections is allowed to drip from the sections before they are hardened at 140°C for 16 to 24 hours. Hardened drippings are rough and then fine-sanded flush with the bottom of the glassy carbon section before the coated glassy carbon sections are mounted in stress relieved* plexiglass stock. Those plexiglass pieces have been turned** to afford centering of the G.C. sections. The sections are then glued in place with an excess of Acme variglas resin and hardener (product #558 and #658 from Acme Chemicals and Insulation Co., New Haven, CT) being careful to avoid any air inclusions or bubbles. This glue is of good optical quality and may be centrifuged to remove air bubbles before using, but stays fluid for only 2 hrs. An excess of this glue must be used as it has a tendency to shrink upon hardening. After initial hardening, this glue may be hardened further by exposure to U.V. light, however, shielding of the upper layers is necessary to afford an even hardening. These hardened, glassy carbon, embedded plexiglass tips are then turned to accommodate electrical contact and centering, then glued to a plexiglass shaft (which has been turned and threaded to accommodate the stainless steel axle), with rohmacrifix-90 plexiglass glue. After hardening, the electrode tip is turned into a bell-shape and the electrode is faced at

* Plexiglass may be stress relieved by placing in an oven at 90°C for 2 hrs or 80°C for 4 hrs.

** To minimize risk of processing contamination, all machine cutting tools should be carbide tipped rather than conventional HSS or Cobalt Steel.

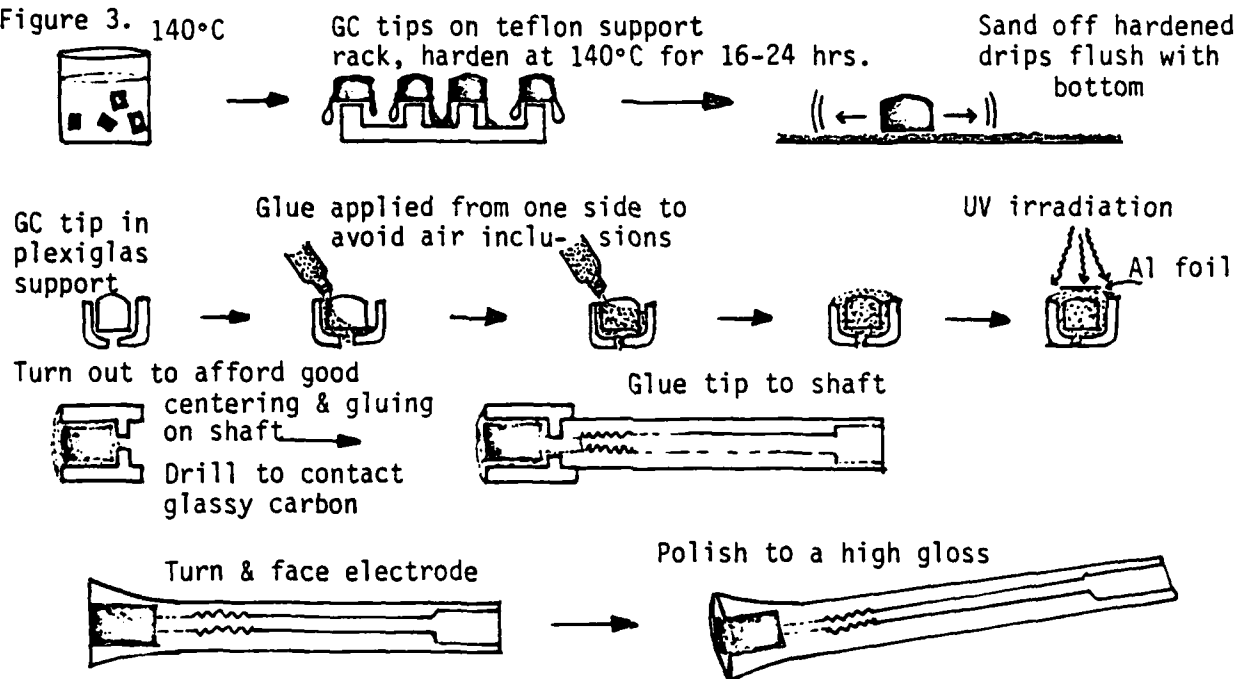
the glassy carbon/Arlidite juncture. The steps in electrode fabrication are illustrated in Figure (3). Polishing of the glassy carbon surface is then initiated with wet sandpaper abrasion of decreasing grain size while the electrode is rotated in a lathe or drill press. Care must be taken not to heat the glassy carbon as the glassy carbon becomes more porous with heating and the differential coefficients of expansion of the materials may lead to fissure formation in the electrode tip. After the finest sandpaper has been applied, the surface is polished manually with diamond polishing compounds applied to wet filter paper decreasing in aggregate size from 25 μm to 3 μm . Care must be taken to clean all traces of aggregate from the electrode before proceeding to a smaller aggregate size. After 3 μm diamond polishing and cleaning the electrode is polished to a high gloss with aluminum oxide applied to wet filter paper. This treatment proceeds in a fashion similar to the diamond polishing, starting with 1 μm aluminum and finishing with .05 μm aluminum. One must not underestimate the importance of the polishing procedure.

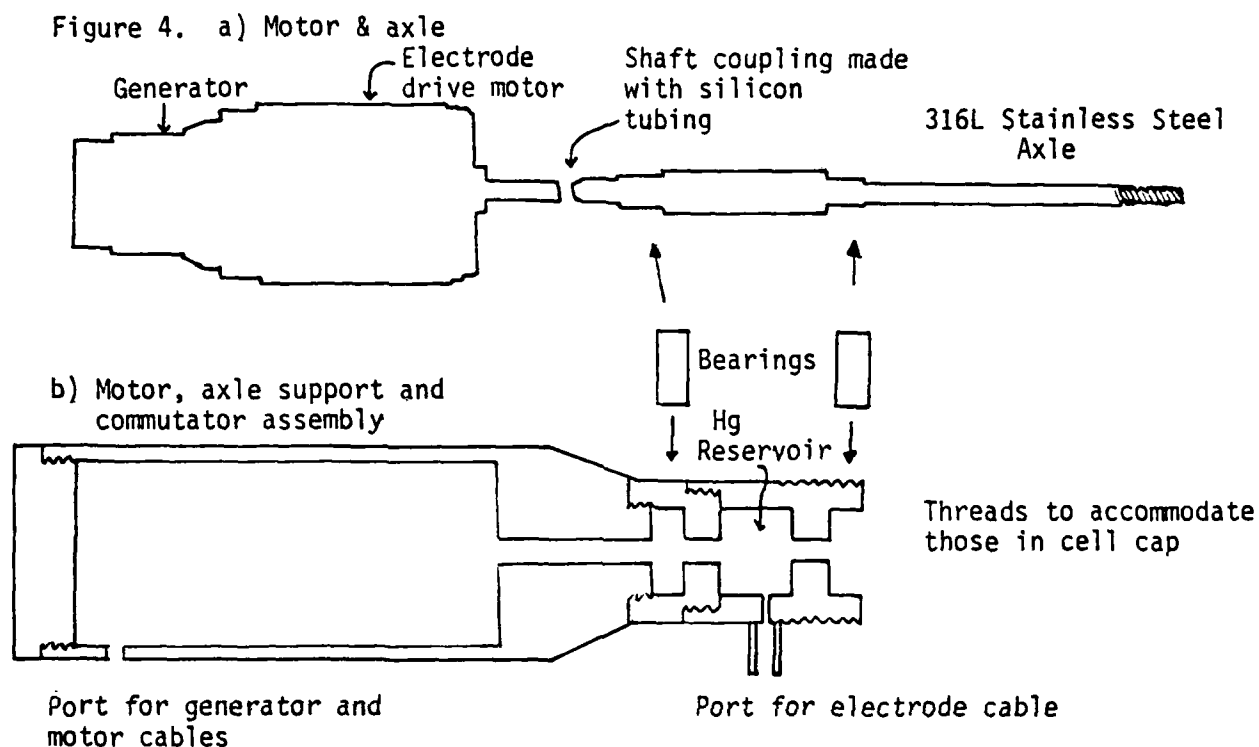
This process is tedious and critical to good electrode performance. Improper polishing leads invariably to high background current, steep hydrogen wave and mercury wave slopes and a reduction in sensitivity.

1d. The Working Electrode Drive Assembly is best described in the form of few drawings (see Figure 4). The electrode is rotated on an axle of 316 L stainless steel and secured by means of the threaded axle tip. Mercury fills the void between the axle terminus and the glassy carbon to afford good electrical contact.

The axle rides on two roller bearings supported within the plexiglass outer motor housing. The motor driving the axle also drives a small generator.

Figure 3. 140°C





The generator output is fed back to the motor power box and processed to regulate motor power supply and insures constant rpm of the electrode. The junction between the motor shaft and axle is made with silicon tubing so that motor noise (due to brushes, etc.) is isolated from the electrode. Between the bearings is a cavity filled with mercury which contacts the axle and a platinum wire affording electrical junction from the axle to the polarograph. It is critical that the tolerances of the axle port do not allow mercury seepage (i.e. port not larger than axle diameter $+0.01$ mm). This entire assembly (motor, bearings, axle and housing) is threaded into the top of the electrochemical cell cap.

2. CELL CONSTRUCTION

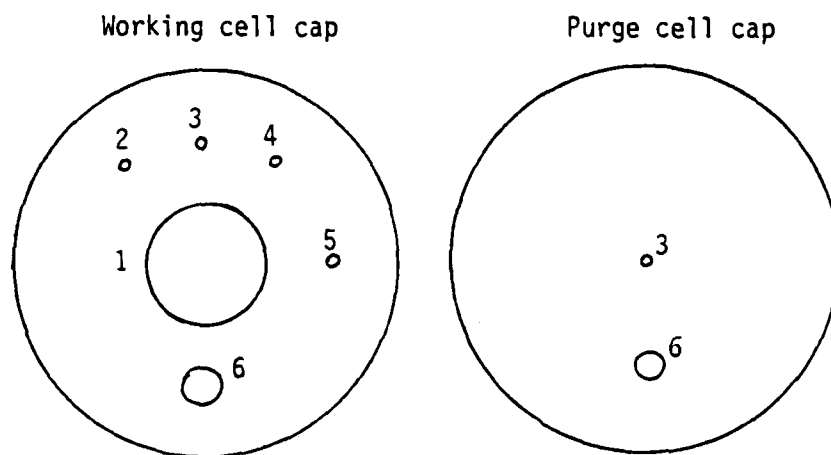
2a. The electrochemical cells and cell caps are made from stress relieved TFE teflon. Again, diagrams best describe their construction (Figure 5), but a few points will be emphasized here. The teflon stock may be stress relieved by heating in an oven to 150°C for 4 hrs before machining. The tools used for turning, boring, and threading of these cells should, wherever possible, be carbide tipped. Persistent and insidious contamination of the cells can result from the use of conventional tools.

2b. Cell caps should be bored to accommodate equidistant placement of working and reference electrodes relative to the counter-electrode. This is accomplished best in a triangle configuration with the working electrode placed in the center of the cell cap and the counter and reference electrodes on either side towards the rear. This electrode configuration ensures accurate potentiostatic alignment of the 3 electrodes as the resistance through the analyte with respect to the counter electrode will be the same regardless of the ohmic resistance of the solution. The port for nitrogen purging of the sample can be bored between the counter and reference electrode ports. A port for the blanketing nitrogen supply may be bored to either side of the working electrode and a port through which standard additions are made, should be made near the front of the cell cap. This configuration, see Figure (5), affords easy access to the working electrode for polishing and servicing as well as unencumbered access for standard additions.

All machined parts which contact the sample must be rigorously cleaned with acid before use. Cells and cell caps are heated in concentrated HNO_3 for a few days before soaking in dilute acid for longer periods of time.

Figure 5.

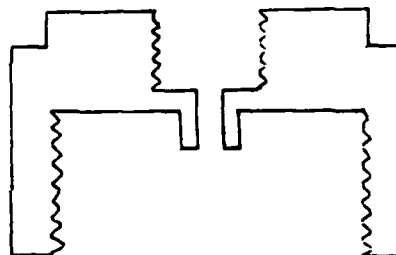
Top view



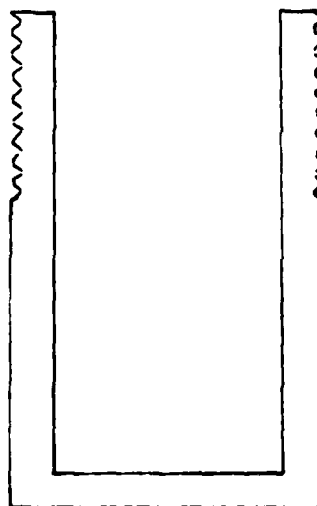
Port designation:

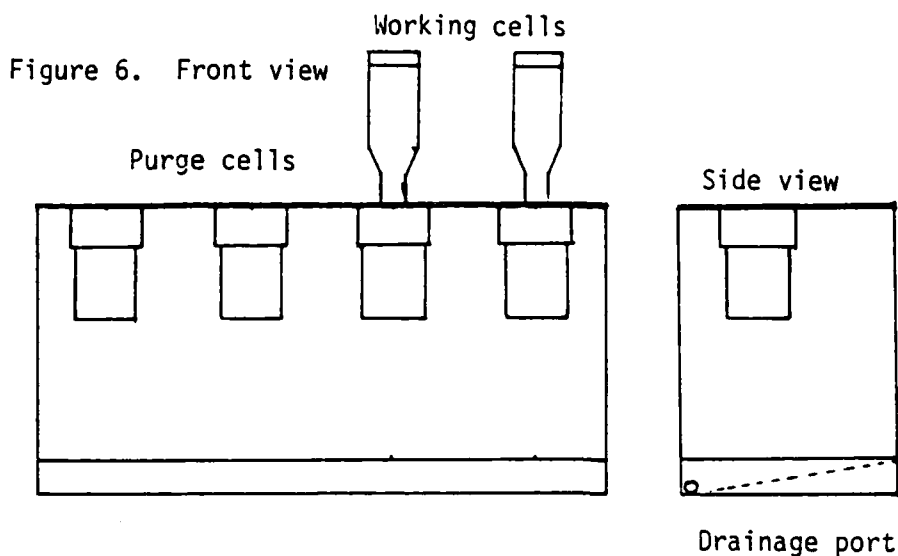
- 1 Working electrode
- 2 Counter electrode
- 3 N₂ Purge supply
- 4 Reference electrode
- 5 N₂ blanket supply
- 6 Standard addition port

Side view



85 ml sample
cell, 50-65 ml
working volume

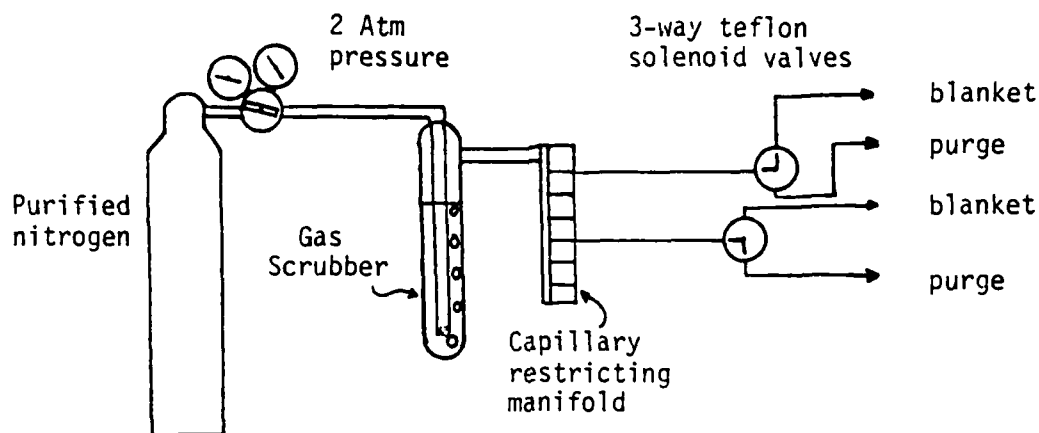




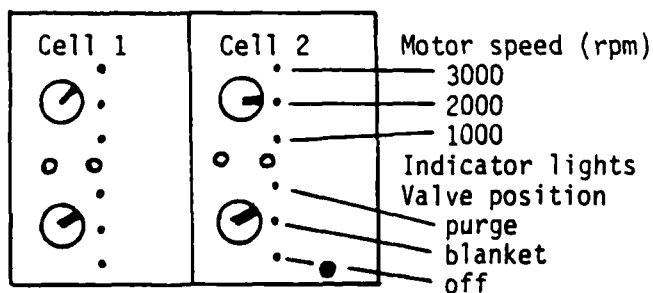
The electrode and deaeration cells pictured in Figure 6 are operated within a clean, laminar flow bench, and separated by cables from the polarograph and chart recorder which are mounted alongside or underneath the cleanbench. The two electrodes can be operated simultaneously with two PAR 174A's [and appropriate chart recorder(s)], or sequentially with one PAR 174A.

2c. The nitrogen used to purge and blanket the samples is high purity grade 99.999% or better. The nitrogen is bubbled through a fritted disc at the bottom of a glass trap (30 mm tall) containing 0.1 N HCl. The gas then passes via silicon tubing to a capillary restricting manifold. From the manifold, the gas passes via teflon tubing to 3-way teflon solenoid valves (1 valve for each electro-chemical cell). In the un-activated position, the nitrogen passes from the valve to teflon tubing supplying the purge port of the electrochemical cell. In the activated position, the nitrogen passes, via teflon tubing, to blanket the sample in the cell. Since blanketing of the sample is needed only during the equilibration and stripping stages, overheating of the valves was avoided (Figure 7). Typically, the

Figure 7.



valves are mounted with the restricting manifold in the motor control box. In this configuration, the motors and the solenoid valves can be activated from a single switch. The switch in one position switches on the electrode driver motor and leaves the solenoid valve unactivated (sample purging). In the other position, the motor is switched off and the solenoid valve is activated (sample blanketing). The control box also has a rotation speed selector switch which enables the operator to choose among 3 speeds (1000, 2000, 3000 rpm), the slowest of which is used for electrode polishing, the intermediate speed used for routine depositions, and the highest used where high sensitivity is required, see Figure (8).



3. INSTRUMENTAL MODIFICATIONS

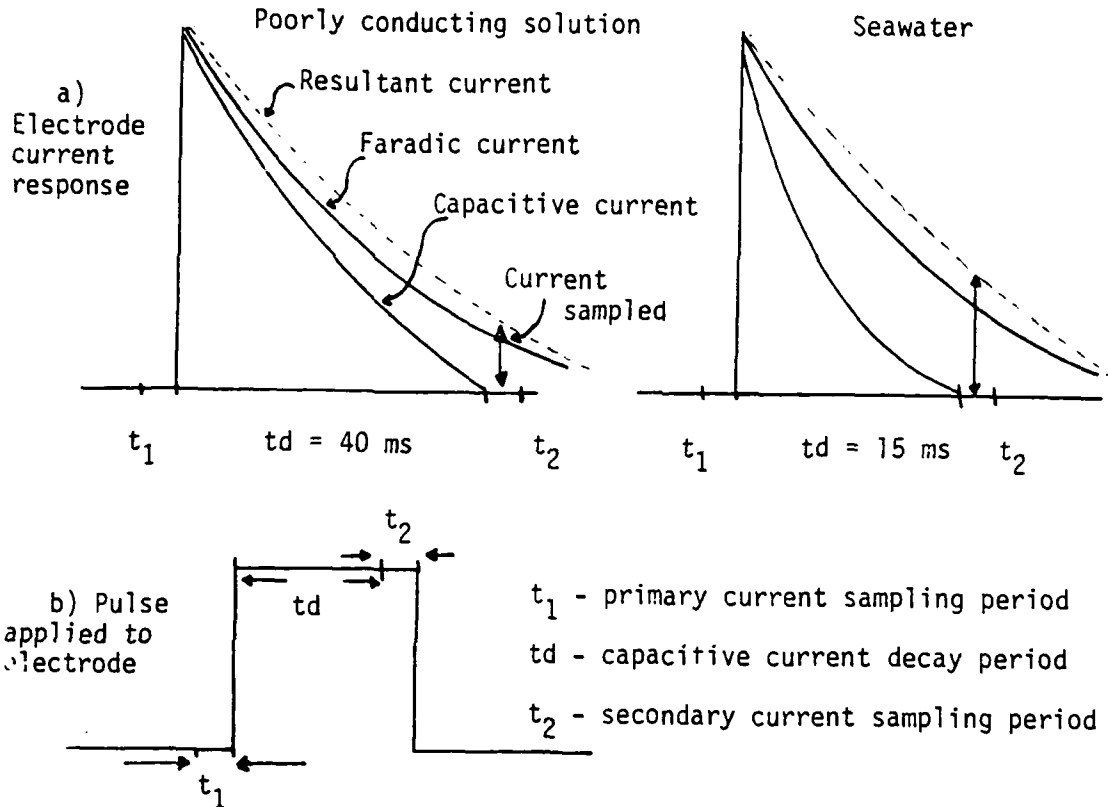
Through the course of our studies at KFA and at NIOZ, we have worked with the research grade polarograph made originally by PAR (and now by EG&G/PARC), the 174 and 174A with a variety of compatible chart recorders. At both institutions, the polarographs were modified to achieve optimal performance with seawater as the analyte. At NIOZ, a switch was installed on the back panel to enable the operator to switch back to original factory specifications. However, due to the increased sensitivity obtained with these modifications, this switch was for comparison purposes only and was not used for the analysis of real samples. A description of these modifications are presented below.

3a. Delay Time

To increase sensitivity, the delay time is shored up from 40 ms to 15 ms. This modification affords maximum differential between faradic currents sampled at t_{s1} and t_{s2} in highly conductive solutions like seawater. A schematic representation of the pulse/current response for two different mediums is given in Figure (9).

Since the capacitive current response decays rapidly in seawater, a greater current difference can be detected by sampling immediately after this decay and before the faradic current has had much time to decay. For seawater, this requires a readjustment of the delay time from 40 to 15 ms. This is accomplished by replacing the 110 K Ω resistor, R-264, in the timing monostable II circuit on the signal processing board with a fixed resistor of 10 K Ω in series with a variable resistor of 0 + 100 K Ω (metal film, 10-turn trim pot). The delay time can be monitored at Test Point (T.P) 208 (td) or the complete pulse may be monitored at T.P. 108

Figure 9.



($t_d + t_2$) and adjusted to the appropriate duration. R-264 and T.P. 208 are shown (in yellow) on the signal processing board schematics (sheet 2 of 2)¹ and on the signal processing board symbolization master. T.P. 108 is shown in yellow on the programmer potentiostat board schematics (sheet 2 of 2) and symbolization master.

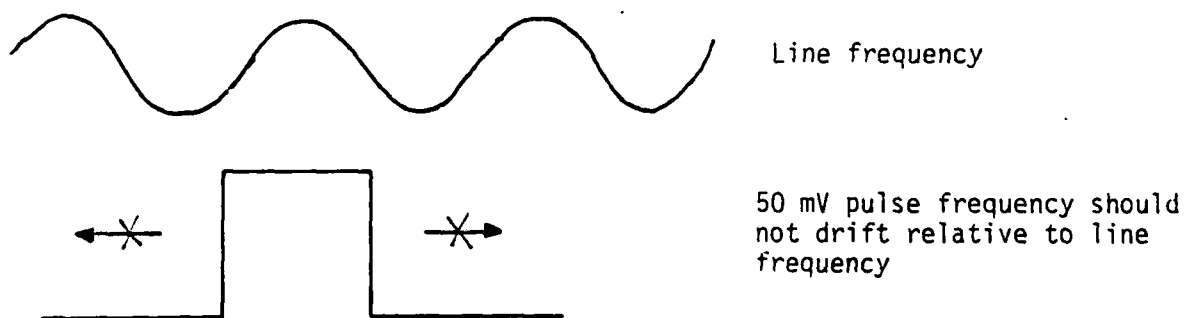
The jumper from T.P.108 to CR 122 is interrupted by the installation of a switch. This switch when opened, prevents the overload detector from truncating the enlarged signals produced from the delay time modification. The switch in closed position restores the circuit to the original factory

¹ Reproductions from the PAR 174 A manual appear appended at the end of this section, with permission from ORTEC/PARC.

conditions. This jumper is shown (in yellow) on the potentiostat board schematics (sheet 2 of 2) and board symbolization master.

3b. Drop Time

The drop time setting of 5 seconds (for the HMDE) was changed to a drop time of 0.24 seconds and synchronized to a multiple of 20 ms. This is the European line frequency period. The drop time should be synchronized to the American frequency (60 Hz) when operating the PAR 174 in the U.S. To accomplish this, the 1 M Ω resistor R-63 on the motherboard is replaced by a 45 K Ω resistor in series with a variable 0 - 5 K Ω resistor (10-turn, metal film). The drop time is then synchronized by adjusting the 10-turn trim pot while monitoring pulse synchrony from T.P. 108 with an oscilloscope. During this adjustment, the PAR selector should be set to "Dummy Cell". The best way to monitor pulse synchrony was to trigger the oscilloscope with a line frequency input (1st trace) and monitor td pulse at T.P. 108 (second trace). Synchrony is obtained when the square wave pulse does not drift relative to the line voltage trace and is stable for 1 minute or so, Figure (10). Figure 10.

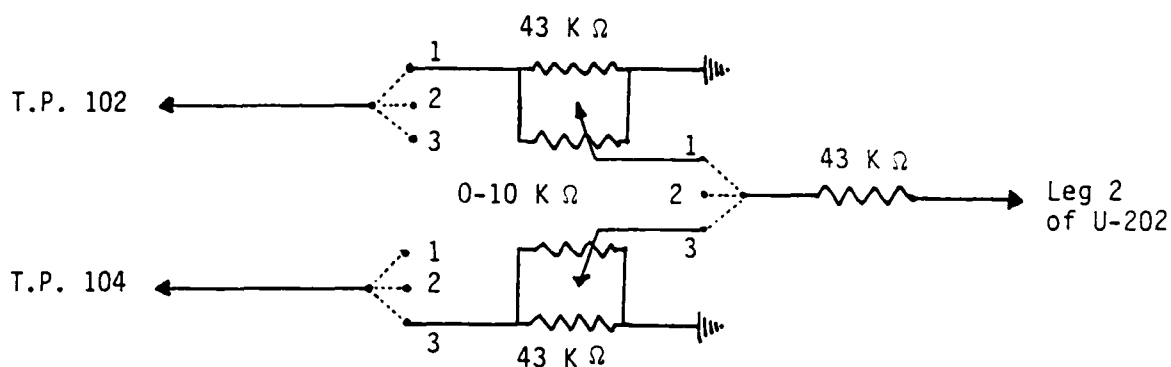


R-63 is shown (in yellow) on chassis wiring diagram and in upper left corner of signal processing board diagram (also shown on motherboard symbolization master. T.P. 108 is shown (in yellow) on programmer potentiostat board schematic (terminus of long yellow line); and on circuit board symbolization master.

3c. Slope Correction Feature

At high sensitivity settings, slope compensation for steep hydrogen reduction and mercury oxidation waves can be achieved by adding a ramping positive or negative voltage to the output amplifier (Pin 2 of U202, signal processing board). Ramping potentials are obtained from ramp generator output T.P. 102 and ramp inverter output T.P. 104 and modified by the following circuit:

Figure 11.



The switch depicted here is a 3-position, 3 pull switch which when in Position 1, will incorporate voltage from T.P. 102, Position 2 is an open circuit and Position 3 incorporates voltage from T.P. 104. The switch and both 10-turn potentiometers are mounted on the front panel of the polarograph. Pin 2 of U-202 is shown (in yellow) on the signal processing board schematics (sheet 1 of 2) and on symbolization master. T.P. 102 and T.P. 104 are shown (in yellow) on programmer-potentiostat board schematics (sheet 1 of 2) and on symbolization master.

3d. The final modification is the placement of a $70\ \Omega$ resistor in series with working electrode. This modification dampens the oscillations of the incorporated potentiostat appearing at the beginning of the pulse when

analyzing highly conductive solutions like seawater. We use a 2-turn 0-100 Ω metal film resistor for this purpose which is adjusted to 70 Ω . The resistor is placed at the working electrode pin connection within the PAR 174.

4. OPERATING PROCEDURE

Described in this section are the instrumental parameters and analytical procedures which we found to yield the best results when analyzing acidified (pH = 2) seawater samples of relatively low metal concentrations by DPASV at the MFE. Slight modifications of this procedure are necessary for other types of samples but will not be discussed here.

Instrumental Parameters

Set the front panel controls of the PAR 174 or 174A to the following positions:

Potential Scan rate	10 mV/sec
Scan direction	⊕ positive
Potential scan range	1.5 volts
Initial potential	-1 volt
Pushbuttons	Initial
Modulation amplitude	50 mv
Operating mode	diff pulse
Selector	Off
Current range	
Rotary switch	.5
Toggle switch	mA
Drop time	.24 sec (Previously 5 sec setting)
Output Offset	
Toggle switch	Off

Instrumental Parameters (continued)

Dial	Fully counterclockwise
Display direction	- negative
Low pass filter	Off
Slope correction:	
Selector switch	Center position (Off)
Dials	Fully counterclockwise
Power	On

Sequence of Polishing and Cleaning Steps Between Samples

1. The glassy carbon electrode is lightly polished with .05 μm alumina on a wetted filter paper, rinsed with ultrapure H_2O , and then a cell with weak ultrapure HCl is put into place and the electrode is rotated in this cleaning solution.
2. The cleaning cell is removed, the electrodes are rinsed with ultra pure H_2O , and the deaerated blank for film formation is put into place.

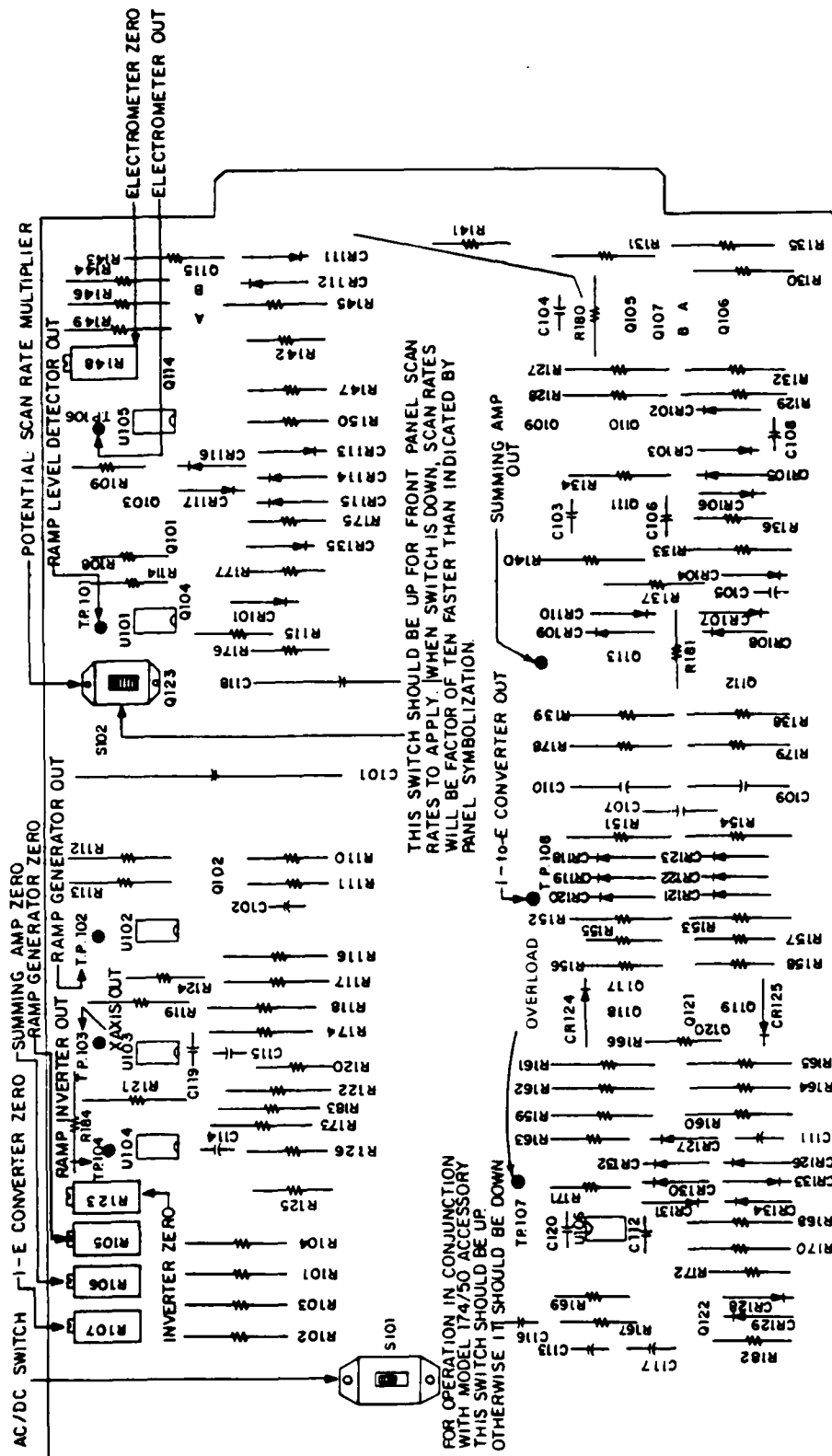
Sequence of Main Operations During Hg Thin-film Formation on The Glassy Carbon Electrode for Acidified Samples

1. 50 ml of ultrapure H_2O acidified to pH 2 (with ultrapure HCl); spike with 100 μl of a 5000 mg.l^{-1} soln of Hg^{2+} ($1.5 \times 10^{-5} \text{m Hg}^{2+}$).
2. Purge with N_2 for deaeration, 10 min.
3. Potential-controlled pre-electrolysis at -1.0 V for 6 min. for film formation; $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}^0$.
4. Stop rotation, adjust start potential to -0.85 V, wait 30 sec.
5. Start potential scan from -0.85 V to =0.1 V in the differential pulse mode, voltammogram is recorded.

6. Clean Hg-film at -0.1 V for 1.5 min. electrode rotates.
7. If the blanks are below 1 ng.kg^{-1} , the system is considered free of contamination, the electrode rotation is stopped, and the blank cell is carefully and quickly replaced with a deaerated sample cell.

Sequence of Main Operations During Voltammetric Analysis for Pb, Cd, and Cu on Acidified Samples

1. A 50^{-60} gm sample acidified to pH 2 (with ultrapure HCl); spike with $\text{Hg}(\text{NO}_3)_2$ (30 μl of a 5000 mg.l^{-1} soln yielding $1.5 \times 10^{-5} \text{ M Hg}^{2+}$).
2. Purge with N_2 for deaeration, 10 min.
3. Transfer cell to electrode position - purge for 2 additional minutes. Potential-controlled pre-electrolysis at -1.0 V for 6 min; glassy carbon electrode with a preformed Hg thin film rotates; $\text{Hg}^{++} + 2\text{e}^- \rightarrow \text{Hg}^0$ (additional film formation); $\text{Me}^{2+} + 2\text{e}^- \rightarrow \text{Me}^0$, $\text{Hg}^0 + \text{Me}^0 \rightarrow \text{Me-analgam}$.
4. Stop rotation, adjust start potential to -0.85 V, wait 30 sec.
5. Start potential scan from -0.85 V to -0.1 V in the differential pulse mode. $\text{Me-analgam} \rightarrow \text{Me}^{2+} + \text{Hg}^0 + 2\text{e}^-$; voltammogram is recorded.
6. Clean Hg-film at -0.1 V for 1.5 min.; electrode rotates;
7. Based upon the signals obtained during the initial 6 min electrode sample conditioning run, choose an appropriate time (e.g. 6 to 30 min) for the Sample run and repeat step 3 to 5.
8. Clean Hg-film at -0.1 V for 1.5 min.; electrode rotates; add known amount of Me^{2+} that approximates the Me^{2+} in the sample.
9. Repeat pre-electrolysis: Step 3 to 5 and 8; however, reduce plating time to one half.
10. Repeat pre-electrolysis: Step 3 to 5; however, reduce plating time to one third.
11. Evaluation of voltammograms.



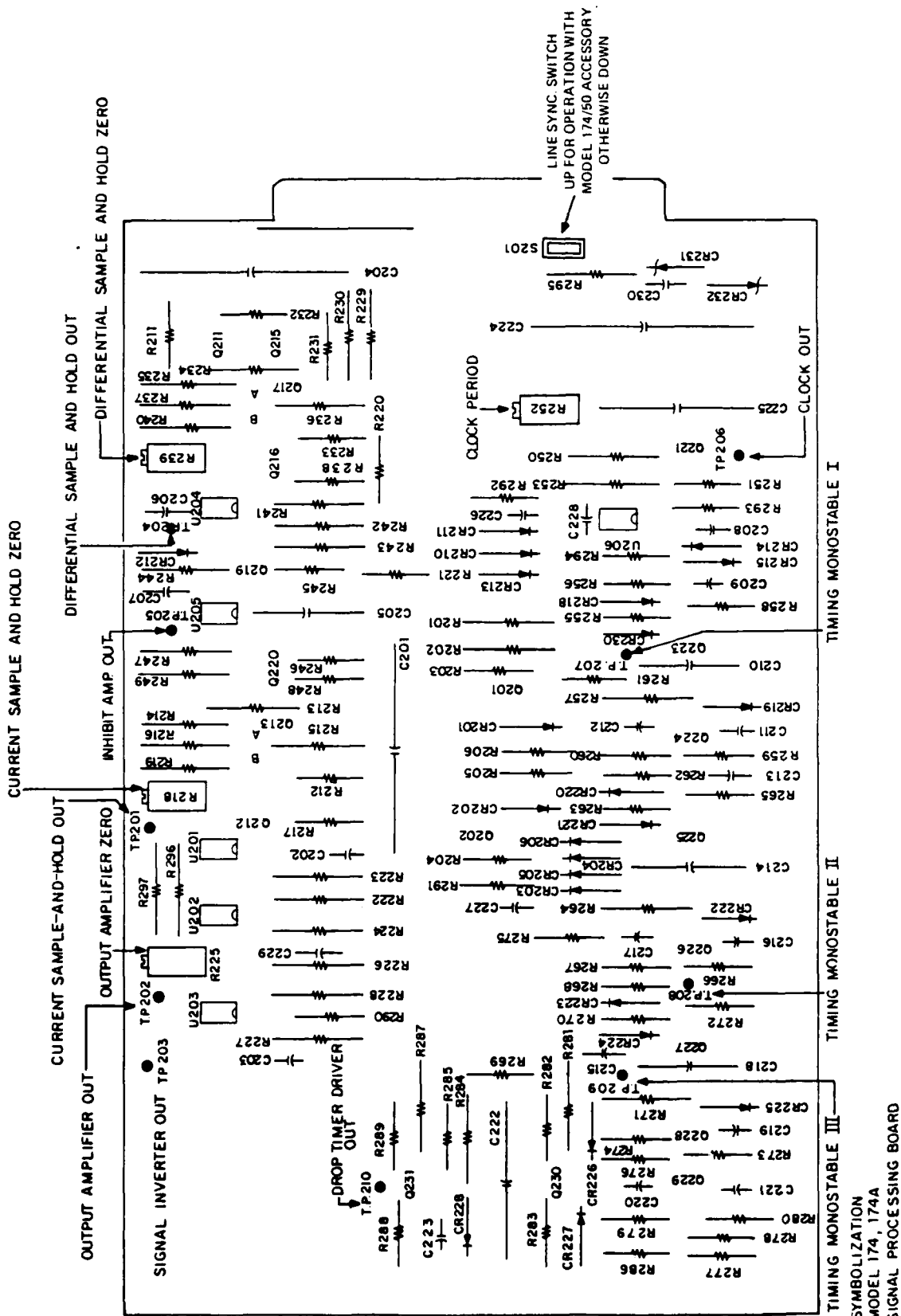
SYMBOLIZATION
MODEL 174, 174A
PROGRAMMER POTENTIOSTAT BOARD

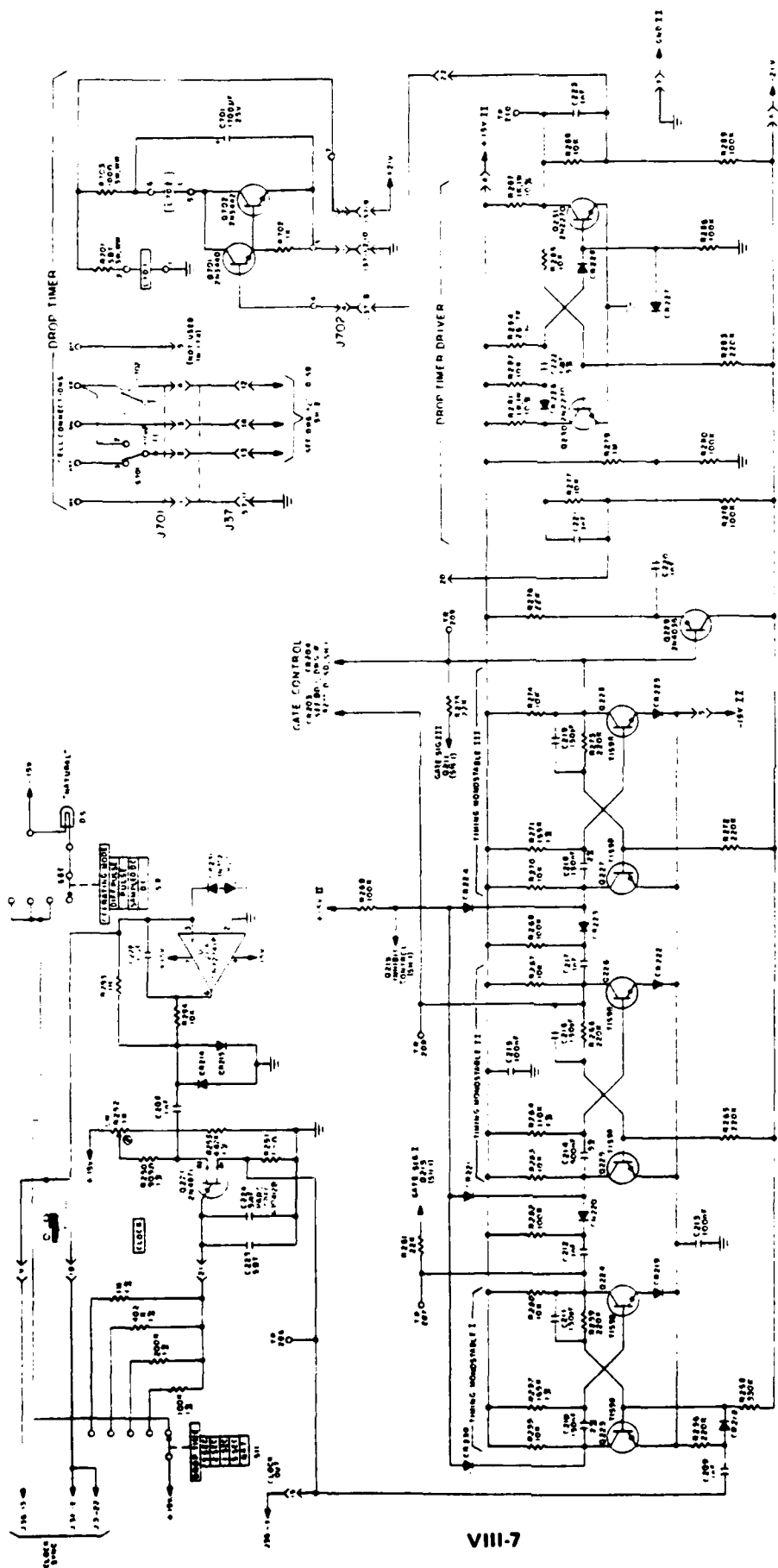
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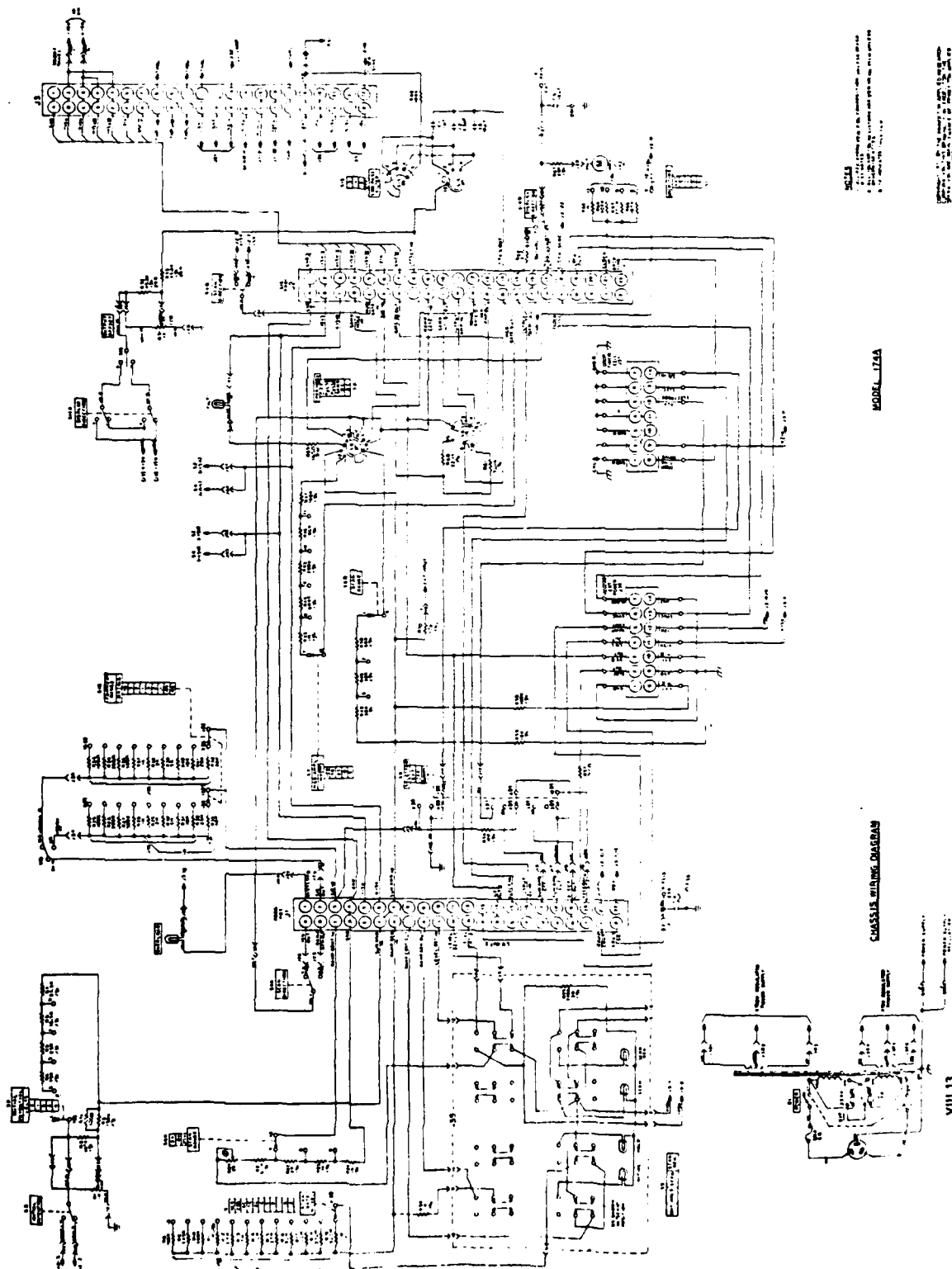


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